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Request for grant of a patent

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1.	Your reference	PP/2268
2.	Patent application number *(The Patent Office will fill in this part)*	9721650.1 — 13 OCT 1997
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	ALCAN INTERNATIONAL LIMITED 1188 Sherbrooke Street West Montreal Quebec CANADA H3A 3G2
	Patents ADP number *(if you know it)*	
	If the applicant is a corporate body, give the country/state of its incorporation	CANADA 3021330[illegible]
4.	Title of the invention	COATED ALUMINIUM WORKPIECE
5.	Name of your agent *(if you have one)*	
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	STEVENS HEWLETT & PERKINS 1 Serjeants' Inn Fleet Street LONDON EC4Y 1LL
	Patents ADP number *(if you know it)*	1545003

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* — Yes

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

COATED ALUMINIUM WORKPIECE

There is a large market in painted aluminium sheet, both for architectural use and for automotive use. There is also a large market for lacquered aluminium sheet for canstock use. In all these applications, the adhesion of the organic coating (typically paint, lacquer or adhesive) to the aluminium metal may not be adequate. Various surface pretreatments have been proposed and are widely used to improve such adhesion:

- An anodic oxide film is formed on the aluminium surface. Particularly when anodising is done in a phosphoric acid based electrolyte, the outer surface of the anodic oxide film may be extremely rough, including filaments or whiskers, such as to provide an excellent mechanical key for subsequently applied organic coatings.
- Adhesion promoters are a class of materials that have been used to improve the adhesion of organic coatings to an underlying metal substrate. One example is polyacrylic acid. A chromium-fluoride-phosphate pretreatment has been successfully marketed under the tradename Accomet C. Other similar treatments contain fluoride values and other transition metals. Such pretreatments may act as adhesion promoters and also provide corrosion resistance.

Adhesion promoters have in general been applied to bare metal. This invention is based on the idea that additional advantages may be obtained if such adhesion promoters are applied to an aluminium metal surface which is not bare.

Thus the invention provides an aluminium workpiece having on a surface thereof an artificially applied aluminium oxide or hydroxide film and a coating which is at least one adhesion promoter.

A workpiece is an object of indeterminate size and shape. While the invention may have application in connection with extrusions and

other workpieces, it is of principal interest in connection with aluminium sheet, either continuous sheet in the form of coil, or cut sheet which is either flat or has been formed into shaped components e.g. for architectural or automotive or canstock use. Depending on the intended application, either one surface or both surfaces of the sheet may have the artificially applied aluminium oxide or hydroxide film and the coating.

The term aluminium is here used to include both the pure metal and alloys in which Al is a major component. Preferred are alloys of the 2000, 3000, 5000 and 6000 series of the Aluminum Association Inc Register.

Preferably the oxide film is an anodic oxide film, e.g. formed by anodising the metal workpiece in an acidic electrolyte. Preferred electrolytes are sulphuric acid, and particularly phosphorus oxyacids including phosphoric acid. Anodising conditions may be chosen, in accordance with criteria well known in the field, to generate an anodic oxide film having a rough outer surface. The artificially applied aluminium oxide or hydroxide film needs to be thick enough to provide abrasion and corrosion resistance; but not so thick as to have a tendency to spall or crack when a workpiece carrying the film is formed to shape; and, in a preferred aspect of the invention discussed below, not so thick as to make the coating so electrically resistant that spot-welding is impossible. Preferred thicknesses are in the range 10 – 200 nm particularly 15 - 150 nm, more especially 15 – 50 nm.

Adhesion promoters are known and employed to enhance adhesive bond strength, or more commonly to enhance the environmental resistance of the substrate surface/adhesive interface to attack by moisture. Adhesion promoters were described by P E Cassidy *et al* in Ind. Eng. Chem. Prod. Res. Development Volume 11, No 2 (1972) pages 170-7; and by A J Kinlock in J Mat. Sci., 15(1980), pages 2141-66 at page 2159. Commercial pretreatments (adhesion promoters) include Alodine NR1453., Alodine NR2010, zirconia/polyacrylic acid, Accomet C

and Safeguard 6000 which contain Ti, Zr, Cr, Mn, Si, F, polyacrylic acid and substituted styrenes.

An adhesion promoter may be an inorganic pretreatment comprising one or more of Cr, Mn, Mo, Si, Ti, Zr values. These can be provided separately. The adhesion promoter may also comprise fluoride values or another acid value. They may conveniently be provided by dissolving fluorozirconic acid H_2ZrF_6, or a soluble fluorozirconate salt, in water; alternatively, a corresponding acid or salt of Cr, Mn, Mo, Si or Ti may be used. Cr is preferably absent on account of its toxicity and effluent problems. Flurozirconate (or other fluoro complex) is preferably present at a concentration of 0.1 – 200 g/l, particularly from 10 – 100 g/l, of a formulation for application to an aluminium workpiece.

In the case of Cr and Mn, there is probably some dissolution of an anodic oxide film and reduction by Al of the Cr or Mn from a higher to a lower oxidation state. In the case of formulations based on Ti or Zr there are no oxidation states to change. It is thought that the hydrofluoric acid may attack the anodic oxide film causing a local pH change resulting in the formation of a pretreatment/Al_2O_3 gel followed by further pretreatment deposition. These inorganic pretreatments may be applied in the form of no-rinse solutions.

Although here described as inorganic pretreatments, these formulations based on fluoride and transition metals may also contain an organic polymer. Whether or not such polymer is present, the inorganic pretreatment coating is preferably provided at a coat weight of 5 - 100 mg/m^2, particularly 10 – 60 mg/m^2.

An adhesion promoter may be organic including one or more silane coupling agents which are organosilanes, for example glycidoxypropyltrimethoxy silane or aminopropyltriethoxysilane, which may act to promote adhesion. Other possible adhesion promoters include siloxanes, polyvinylphenols, polyacrylic acids and salts and esters thereof, and polyacrylic acid/zirconia mixtures. These adhesion promoters are

preferably present at a coat weight of 5 –100 mg/m^2 preferably 10 – 60 mg/m^2. While adhesion promoters are effective to improve surface properties of the aluminium workpieces of this invention, it is surprisingly found that lower concentrations are sometimes more effective than higher concentrations.

In another aspect the invention provides a method of treating an aluminium workpiece, which method comprises precleaning a surface of the workpiece, anodising the workpiece so as to form an anodic oxide film on the surface, and applying an adhesion promoter to the anodic oxide film on the surface. The adhesion promoter is preferably applied, either as a no-rinse coating, e.g. a composition consisting essentially of the adhesion promoter in a volatile vehicle which evaporates from the surface of the workpiece leaving a film of the adhesion promoter without the need for rinsing. Or a conversion coating composition may be used which reacts chemically with the substrate, e.g. the artificial oxide layer, to form a film of the adhesion promoter which is not removed by rinsing.

In one embodiment, a porous anodic oxide film is formed of thickness preferably 50 – 200 nm. When polyacrylic acid or other adhesion promoter is applied on top of the porous film, it generally fills the pores and forms a continuous layer on top of them. This embodiment has surprisingly good corrosion resistance and is particularly suitable as painted sheet for architectural use.

In another embodiment, a barrier layer anodic oxide film is formed of thickness preferably 20 – 50 nm. A pretreatment e.g. NR1453 (adhesive promoter) is applied over this; the anodic film is sometimes found to be thinner after application of the pretreatment but never disappears altogether. A paint film, e.g. a conductive paint primer may be applied over the pretreatment. Sheet according to this embodiment may have surprisingly good forming characteristics and is particularly suitable for automotive use. Components formed from the sheet can be painted on an electroconductive paint line.

The aluminium sheet or other workpiece according to this invention preferably carries on its surface a composite coating consisting of an anodic aluminium oxide film and a coating consisting of an adhesion promoter overlying the film or occupying pores adjacent the outer surface of the film. This composite coating is found to improve adhesion to the workpiece of an applied organic coating such as a paint, lacquer, varnish, enamel or adhesive. In another aspect, the invention provides such an aluminium workpiece where paint, lacquer, varnish, enamel or adhesive is present overlying the artificially applied aluminium oxide or hydroxide film and the adhesion promoter coating.

Within this inventive concept, two embodiments are of particular economic importance. One is painted sheet for architectural use. The other is primed sheet for automotive use. The primer is a paint coating which may be conventional and which is preferably electrically conducting so as to permit electrocoating to be performed. Primed aluminium sheet is widely sold for automotive use, where the presence of the primer gives the sheet improved forming properties.

EXAMPLE 1

Sheets of AA6016, 1.2 mm thick, and AA5182, 1.15 mm thick, were electrolytically cleaned in 200 g/l phosphoric acid at 90°C for 3 seconds at 3 kA/m^2. Half of the sheets were anodised in phosphoric acid to produce a film typically 15 – 50 nm thick. Treatment conditions were:

Phosphoric acid 200 g/l

Temp 65°C

Time 0.5 secs

Spray rinse in 30–50 g/l phosphoric acid then deionised water

Dry 120°C for 2 mins.

After rinsing and drying, the bare and anodised sheets were coated with a Ti containing no-rinse pretreatment Alodine NR 1453 to give a coating weight 5 – 15 mg/m^2 expressed as the weight of Ti. Alodine

NR1453 contains F and Ti, and has in addition a polymer present (a polyvinylphenol).

Comparison samples were prepared by applying a Cr containing no-rinse treatment, Accomet C, at conventional levels.

After drying the sheets were coated on one side with electro conducting epoxy based paint Bonazinc 2004, (containing Al pigment) or Bonazinc 2000 (containing Al/Zn pigments). Coating thickness was about 7±2 microns.

Formability Tests

Formability was measured by means of an Erichsen dome test BS 3855 arranged so that the paint film on the convex side of the dome was extended 20% in biaxial tension. This corresponds to a bulge height of 8 mm. The coating area deformed by the dome was cross hatched. The punch side of the sheet was lubricated. Adhesion in the domed area was measured by means of BS 3900 Part 2 test using a sticky tape. Scoring was as per the BS 3900 Part 2 test in which the best result is 0 and the worst is 5.

The results are presented in Table 1 from which it can be seen that:

1. In the absence of an anodised film the NR1453 was inferior to Accomet C. Performance generally improved as the coating weight decreased.

2. In the presence of an anodised film the NR1453 gave results comparable to or better than Accomet C.

Adhesive Bonding Tests

Sheets prepared as described above were adhesively bonded and tested in T-Peel. 25 mm wide strips were overlapped and adhesively bonded with an epoxy adhesive XD4600, the coated side being towards the adhesive. The overlapped joint was then peeled apart at a cross head

movement rate of 20 mm/min.

On initial application of the peel load, the load rises to a peak and then drops to a constant level as the joints begins to separate. The constant load is measured and must exceed 7N/mm of width of joint. The results are presented in Table 1.

All of the NR 1453 equalled or exceeded 7N/mm when applied to pretreated anodic film.

Table 1 – Automotive Primer Evaluation – Phase II

Alloy	Additional Treatment	Pretreatment	Erichsen (Gt) 8mm Dome	T-Peel (N/mm)
AA 6016	None	Alodine NR 1453 (≈5 mg/m^2)	2	7
		Alodine NR 1453 (≈10 mg/m^2)	4	7-8
		Alodine NR 1453 (≈15 mg/m^2)	4	7-8
		Accomet C	1	
	Anodised	Alodine NR 1453 (≈5 mg/m^2)	1	8
		Alodine NR 1453 (≈10 mg/m^2)	1	7-8
		Alodine NR 1453 (≈15 mg/m^2)	2	7-8
		Accomet C	2	7-8
AA 5182	None	Alodine NR 1453 (≈5 mg/m^2)	2	
		Alodine NR 1453 (≈10 mg/m^2)	3	
		Alodine NR 1453 (≈15 mg/m^2)	5	
		Accomet C	2	
	Anodised	Alodine NR 1453 (≈5 mg/m^2)	1	9
		Alodine NR 1453 (≈10 mg/m^2)	0	8
		Alodine NR 1453 (≈15 mg/m^2)	1	8
		Accomet C	1	

EXAMPLE 2

The conditions of Example 1 were reproduced using a production line comprising an electrolytic etch, anodising to form a barrier layer about 20 nm thick, to which the pretreatment was applied by roller coating at 60 m/min. Erichsen test bulges were made having a height of 8 mm. Results are summarised in Table 2.

On both alloys the presence of a barrier film under the pretreatment improved performance.

Table 2 – Primer Applications – Summary of Erichsen Dome Test Adhesion Performance

Surface Cleaning	Pretreatment	Paint	Bonazinc 2000		Bonazinc 2004	
		Alloy	6016	5182	6016	5182
		Dome Height (nm)	8	8	8	8
Electrolytic etch	Alodine NR 1453		3	4	2	4
≈20 nm barrier layer (anodised)	None		3	3	2	3
	Alodine NR 1453		1	2	2	0

EXAMPLE 3

Aluminium sheet intended for use as closure stock for cans was anodised in sulphuric acid on a commercial production line run at two different speeds of 40 m/min (slow) and 90 m/min (standard). Some of the anodised sheet was then treated with either polyacrylic acid (MW 60000 PAA) or an amino silane (silane). Panels were then bar coated with two white polyester external enamels plus clear overprint varnishes using normal commercial practices. 60 mm deep drawn shells were produced from the lacquered panels lubricated with caster oil, again in accordance with normal commercial practice. The following lacquer adhesion tests were performed..

Feathering Test

At the closure base a small cup was extended round the shell circumference. The relative lacquer feathering characteristics for each experimental substrate were assessed by comparing with specimen standards, and ranked on a scale 0 to 4 with the highest value showing the worst coating adhesion.

Cross-hatch adhesion loss

At the closure base where the coating had received the most deformation, grid lines were scored through the lacquer into the panel using a metal scribe. Lacquer adhesion was assessed by firm application of adhesive tape on to the grid lines, followed by quick removal and the film percentage adhesion loss estimated and performance ranked on a scale 0 to 4.

Adhesion after Autoclaving

Closures were immersed in water held at 120°C for 30 mins in an autoclave, and the lacquer adhesion characteristics were assessed.

The results are set out in Table 3. It can there be seen that both PAA and silane improve the performance of the coating.

Table 3 - Lacquer Adhesion Characteristics

Substrate Identification		Lacquer Performance			
Trial	Anodising: (m/min)	Feathering Test	Cross-hatch Adhesion Loss	Adhesion after Autoclaving	Total Score
I	Std: 90	0	1	0.5	1.5
	Slow: 40	0.5	0.5	0	1
	Std: 90 + PAA	0	0	0	0
II	Std: 90	0	3	0	3
	Std: 90+ Silane	0	0.5	0.5	1
	Slow: 40 + Silane	0	0	0	0

EXAMPLE 4

Two alloys were used in this work, AA3005 which was 0.4 mm thick, and AA5754 which was 0.95 mm thick. Panels of each alloy were precleaned by treatment with phosphoric acid for 3 seconds at 90°C. They were then anodised in phosphoric acid at 65°C using a current of 3 A. In some cases the anodised surfaces were given further treatment with adhesion promoters:-

Accomet C, a commercial no rinse treatment based on hexavalent chromium and containing fluoride and phosphate values;

1:1 by weight mixtures of zirconium oxide and polyacrylic acid;

Polyacrylic acid alone;

An amino silane.

The pretreated specimens were then painted and exposed to acid salt spray according to DIN 50021-ESS. Results set out in Table 4 below are expressed on a scale of 0 to 5 where 0 is excellent, 1 and 2 are acceptable, 3 is borderline and 4 and 5 are unacceptable. The alloy here was AA3005. Paint A was a single coat polyester. Paint B was a 2-coat polyester system.

Table 4

Paint	Anodised (secs)	Adhesion Promoter	Hours exposed to acetic acid salt spray			
			Panel & Scribe		Creep	
			336	1008	336	1008
A	2	-	4	X	1	X
A	2	Accomet C	1	2	1	1
A	2	Zr:PAA	3	4	4	5
A	2	PAA	1	2	1	5
A	2	Silane	2	5	1	3
B	2	-	4	X	1	X
B	2	Accomet C	1	2	1	3
B	2	Zr:PAA	2	3	1	1
B	2	PAA	1	2	1	5
B	2	Silane	2	3	1	1

X = Test discontinued

Anodic film thicknesses were determined from TEM micrographs. The anodising parameters used and the resulting pretreatment thicknesses are summarised in Table 5 below.

Table 5

Anodising Parameters		Anodic Film Thickness (nm)		Additional Pretreatment	
Temp. (°C)	Time (Secs)	Barrier	Total	Adhesion Promoter	Thickness (nm)
65	2	40	80	None	None
		35	80	Accomet C	25
		40	80	1:1 Zr:PAA	40
		40	100	PAA	-
		40	80	Silane	110

EXAMPLE 5

Panels of the same alloys as used in Example 4 were precleaned for 3 seconds in phosphoric acid at 65°C using an anodising current of 3 A. The anodising process time was varied to produce either a 30 nm barrier layer or a 100 nm fully filamented anodic film. Some anodised panels were additionally treated with polyacryclic acid (PAA) or polyvinylphenol solutions at two different spin coating concentrations. The treated panels were painted with a base coat and a clear coat, cured, and exposed to acetic acid salt spray tests (DIN 50021). The experiments are summarised in the following Table 6 and the results given in Table 7. The findings can be summarised:-

1. Phosphoric acid anodised pretreatments gave poor acetic acid salt spray test irrespective of anodic film structure.

2. The acetic acid salt spray test performance of the phosphoric acid anodised pretreatment was significantly improved by subsequent treatment with PAA or polyvinylphenol solutions. A 2% PAA spin coated application produced the best overall performance and without any failures.

Table 6

Expt	ALLOY	ANODISING PARAMETERS			ADDITIONAL PRETREATMENT	Spin Coating % Conc.
		Amps	Temp. (°C)	Time (secs)		
1	AA3005	3	65	1.5	None	
2				3		
3					PAA	0.5
4						2
5					PVP	0.5
6						2
7	AA5754	3	65	1.5	None	
8				3		
9					PAA	0.5
10						2
11					PVP	0.5
12						2

Table 7

Hours exposed to acetic acid salt spray (DIN 50021)									
Expt.	Panel & Scribe			Bend			Creep		
	336	504	1008	336	504	1008	336	504	1008
1	4	4	5	5	5	5	1	1	5
2	4	4	5	2	2	5	1	1	5
3	1	1	2	2	2	2	1	1	1
4	1	1	2	2	2	2	1	1	1
5	1	1	2	1	3	3	1	1	1
6	1	1	2	1	1	2	1	1	1
7	4	4	5	2	2	5	1	1	5
8	4	4	4	1	1	1	1	1	5
9	1	1	3	1	1	1	1	1	1
10	1	1	1	1	1	1	1	1	1
11	1	1	1	1	1	5	1	1	3
12	1	1	1	1	2	4	1	1	3

CLAIMS

1. An aluminium workpiece having on a surface thereof an artificially applied aluminium oxide or hydroxide film and a coating which is at least one adhesion promoter.

2. An aluminium workpiece as claimed in claim 1, which is aluminium sheet of which at least one surface has the artificially applied aluminium oxide or hydroxide film and the coating.

3. An aluminium workpiece as claimed in claim 1 or claim 2, wherein the artificially applied aluminium oxide or hydroxide film is an anodic oxide film.

4. An aluminium workpiece as claimed in any one of claims 1 to 3, wherein the artificially applied aluminium oxide or hydroxide film is 10 - 200 nm thick.

5. An aluminium workpiece as claimed in any one of claims 1 to 4, wherein an adhesion promoter contains one or more of Cr, Mn, Mo, Si, Ti and Zr values.

6. An aluminium workpiece as claimed in any one of claims 1 to 5, wherein an adhesion promoter is selected from silanes, siloxanes, polyvinylphenols, polyacrylic acids and salts and esters thereof and polyacrylic acid/ZrO_2 mixtures.

7. An aluminium workpiece as claimed in any one of claims 1 to 6, wherein the adhesion promoter coating is present at a weight of 5 - 100 mg/m^2.

8. An aluminium workpiece as claimed in any one of claims 1 to 7, wherein a paint, lacquer, varnish, enamel or adhesive is present overlying the artificially applied aluminium oxide or hydroxide film and the adhesion promoter coating.

9. An aluminium workpiece as claimed in claim 8, which is painted sheet for architectural use.

10. An aluminium workpiece as claimed in claim 8, which is primed sheet for automotive use.

11. A method of treating an aluminium workpiece, which method comprises precleaning a surface of the workpiece, anodising the workpiece so as to form an anodic oxide film on the surface, and applying an adhesion promoter to the anodic oxide film on the surface.

12. A method as claimed in claim 11, wherein the adhesion promoter is applied as a no-rinse coating or a conversion coating.